

NPS ARCHIVE  
1965.06  
BALLOU, J.

AN EXPERIMENTAL DETERMINATION OF THE  
PARAMETER OF NONLINEARITY FOR FOUR  
INDIUM-BISMUTH MOLLEN ALLOYS

JOSEPH FRANK BALLOU

**DUDLEY KNOX LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CA 93943-5101**









An Experimental Determination of the Parameter of  
Nonlinearity for Four Indium-Bismuth Molten Alloys

by

Joseph Frank Ballou

B.Sc., United States Naval Academy, 1957

Thesis

submitted in partial fulfillment of the requirements for the  
Degree of Master of Science in the Department of  
Physics at Brown University

June, 1965

~~Thesis~~  
~~B201~~

NPS ARCHIVE

1965.06

BALLOU, J.



DUDLEY KNOX LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CA 93943-5101

11

This thesis by Joseph Frank Ballou is accepted in its present form by the Department of Physics as satisfying the thesis requirement for the degree of Master of Science.

Date: . . . . .

Approved by the Graduate Council

Date: . . . . .



# Table of Contents

	<u>Page</u>
I. Introduction . . . . .	1
II. Experimental Equipment and Procedure . . . . .	6
A. Method of measuring sound velocity . . . . .	6
B. Description of equipment . . . . .	7
1. Pressure system . . . . .	8
2. Temperature control and measurement . . . . .	8
3. Electronic system . . . . .	8
4. Pressure vessel and components . . . . .	11
5. List of equipment . . . . .	13
C. Preparation of experimental apparatus and sample . . . . .	15
D. Equilibrium conditions . . . . .	18
E. Measurement of repetition rate and temperature . . . . .	18
III. Corrections and Calibrations . . . . .	20
A. Delay line corrections . . . . .	20
B. Superposition corrections . . . . .	21
C. Waveguide effect corrections . . . . .	23
D. Viscosity corrections . . . . .	24
E. Temperature errors . . . . .	25
F. Calibrations . . . . .	25
IV. Data . . . . .	26
A. Sample calculations for velocity of sound . . . . .	26
B. Velocity of sound tables . . . . .	31
C. Computation of $B/A$ . . . . .	37
V. Conclusions . . . . .	45
References . . . . .	53



Acknowledgment

I would like to express my appreciation to Professor Robert T. Beyer for his interest and advice in the preparation and execution of this work. Also, I would like to express by thanks to Mr. Alan Coppens for his help on the experimental apparatus.



## I. Introduction

In studies of the propagation of finite amplitude sound waves in liquids, recourse is generally made to the so-called non-linear parameter  $B/A$ , which can be defined by an expansion of pressure changes in terms of density changes in the liquid for an isentropic process. If we use a Taylor expansion for this relation

$$p = p_0 + \left(\frac{\partial p}{\partial \rho}\right)_{0,s} (\rho - \rho_0) + \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{0,s} \frac{(\rho - \rho_0)^2}{2} + \dots \quad (1)$$

where  $p, p_0$ , are the instantaneous and hydrostatic pressures,  $\rho, \rho_0$ , the instantaneous and equilibrium densities, where the derivatives are taken at  $\rho = \rho_0$  and constant entropy, and limit ourselves to terms through quadratic, we can rewrite the equation as

$$p = p_0 + A \frac{\rho - \rho_0}{\rho_0} + \frac{B}{2} \left(\frac{\rho - \rho_0}{\rho_0}\right)^2. \quad (2)$$

Since the first derivatives is the square of the infinitesimal sound velocity,  $c_0^2$ ,  $A = \rho_0 c_0^2$ , and we can write the ratio

$$\frac{B}{A} = \frac{\rho}{c_0^2} \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{0,s}. \quad (3)$$

There are three principal method of determining  $B/A$ ;

- 1) Finite Amplitude Determination,
- 2) Static Determination, and
- 3) Thermodynamic Determination.

### Finite Amplitude Determination

This method makes use of the harmonic distortion in a propagated wave. The amplitude of the second harmonic is compared to the amplitude of the first harmonic. There are several





different experimental approaches to the problem.

Shklovskaya-Kordi<sup>1</sup> used an acoustic filter to filter out the second harmonic and a quartz receiver to obtain data. Adler and Hiedemann<sup>3</sup> used the same arrangement except that the measurements were taken by determining the variation of the index of refraction of the liquid instead of using a receiver. Various other experimental techniques are discussed by L.K. Zarembo and V.A. Krasil'nikov.<sup>2</sup>

Some problems associated with the above method are that the filter employed may interact with the system, and if it passes second harmonic waves then it passes the fourth harmonic also. Reflections may also be a problem especially if an acoustic receiver is used. Theoretically, the equations concerned with finite amplitude are difficult to manipulate and, in some cases, cannot be solved without approximations on the non-linear effects.

### Static Determination

A static determination of  $B/A$  requires precise measurements of density as a function of pressure at constant temperature. The data is analyzed for the slope and derivative of the slope of specific volume with respect to pressure. This information will provide the non-linear parameter of the isothermal equation of state. The difference between this parameter and the isentropic non-linear parameter has been investigated by Coppens.<sup>4</sup> While the difference is quite small, accurate measurements of the thermodynamic parameters needed to calculate this difference are almost nonexistent.

The main difficulty with this method of determining  $B/A$  is that very accurate data are required as the two derivatives are



about equal and are subtracted from each other.

### Thermodynamic Method

This method involves measuring the velocity of sound and its derivatives with respect to pressure and temperature. Because of the simplicity of this measurement compared to the other determinations, the thermodynamic method was chosen for use in this research.

There are two devices which measure the velocity of sound with the accuracy desired, the velocimeter and the interferometer. The velocimeter was chosen, as the interferometer, because of its movable parts, would require elaborate seals to contain the pressures required.

To establish the thermodynamic method, we rewrite equation (3).

$$\frac{B}{A} = \frac{\rho_o}{c_o^2} \left( \frac{\partial^2 p}{\partial p^2} \right)_{o,s} = \frac{\rho_o}{c_o^2} \left( \frac{\partial c_o^2}{\partial p} \right)_{o,s} = 2\rho_o c_o \left( \frac{\partial c_o}{\partial p} \right)_{o,s}$$

the differential  $dS$  can be written:

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

Using Maxwell's relations, we recast the above equation in the form

$$TdS = C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP$$

For an isentropic process

$$dT = \frac{T}{C_P} \left( \frac{\partial V}{\partial T} \right)_{P,S} dP$$



Now

$$\begin{aligned} dc &= \left(\frac{\partial c}{\partial p}\right)_{T,S} dp + \left(\frac{\partial c}{\partial T}\right)_{P,S} dT + \left(\frac{\partial c}{\partial S}\right)_{T,P} dS \\ &= \left(\frac{\partial c}{\partial p}\right)_{T,S} dp + \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_{P,S} \left(\frac{\partial c}{\partial T}\right)_{P,S} dp + \left(\frac{\partial c}{\partial S}\right)_{T,P} dS \\ \left(\frac{\partial c}{\partial p}\right)_S &= \left(\frac{\partial c}{\partial p}\right)_{T,S} + \frac{\beta VT}{C_P} \left(\frac{\partial c}{\partial T}\right)_{P,S} \end{aligned}$$

where  $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,S}$

Substituting the above expression in equation (3), we obtain

$$\begin{aligned} \frac{B}{A} &= 2\rho_0 c_0 \left[ \left(\frac{\partial c}{\partial p}\right)_{T,S} + \frac{\beta VT}{C_P} \left(\frac{\partial c}{\partial T}\right)_{P,S} \right] \\ &= 2\rho_0 c_0 \left(\frac{\partial c}{\partial p}\right)_{T,S} + \frac{2c_0 \beta T}{c_p} \left(\frac{\partial c}{\partial T}\right)_{P,S} \quad (3a) \\ &= (B/A)' + (B/A)'' \end{aligned}$$

where  $c_p = \frac{C_P}{\rho V}$ .

Thus we have an equation where the components can be experimentally determined.

The assumption that sound transmission is isentropic has been investigated by Gol'dberg.<sup>5</sup> He showed that if the absorption of sound is small over a wavelength (i.e.,  $\alpha/k \ll 1$ ) and

$$\frac{\omega \kappa \left(1 - \frac{c_V}{c_P}\right)}{\rho c_V c^2} \ll 1$$

then

$$\frac{(\partial p / \partial s)_0 (s - s_0)}{(\partial p / \partial p)_s (p - p_0)} = \frac{\omega \kappa \left(1 - \frac{c_V}{c_P}\right)}{\rho c_V c^2}$$





where  $\alpha$  is the absorption coefficient,  $k$  the wave number,  $\omega/2\pi$  the frequency,  $\kappa$  the coefficient of thermal conductivity,  $c_v(c_p)$  the heat capacity for constant volume (pressure),  $\rho$  the density, and  $c$  the velocity of sound. In most liquids the absorption coefficient  $\alpha$  is sufficiently small to satisfy Gol'dberg's requirements and in the present case experimental observation indicates that  $\alpha$  is sufficiently small here also.

$$\frac{\omega\kappa(1 - \frac{c_v}{c_p})}{\rho c_v c^2} \approx 2 \times 10^{-5} \ll 1$$

for the liquids investigated. Coppens<sup>30</sup> also shows that higher order terms and the cross terms of the complete Taylor expansion are negligible.





## II. Experimental Equipment and Procedure

### A. Method of measuring sound velocity.

The method used for the measurement of sound velocity in this research was the velocimeter method of Greenspan and Tschiegg<sup>6</sup> as adapted by Coppens.<sup>7</sup> The sample was contained in a cylindrical tube each end of which was terminated by a 5 Mc/s quartz crystal for the transmission and reception of sound pulses. A knowledge of the repetition rate of the sound pulses is sufficient to determine the time required for a sound pulse to travel the length of the velocimeter. When the length of the velocimeter is accurately known the velocity can be determined.

The principle of the timing method can be understood by means of Fig. 1.

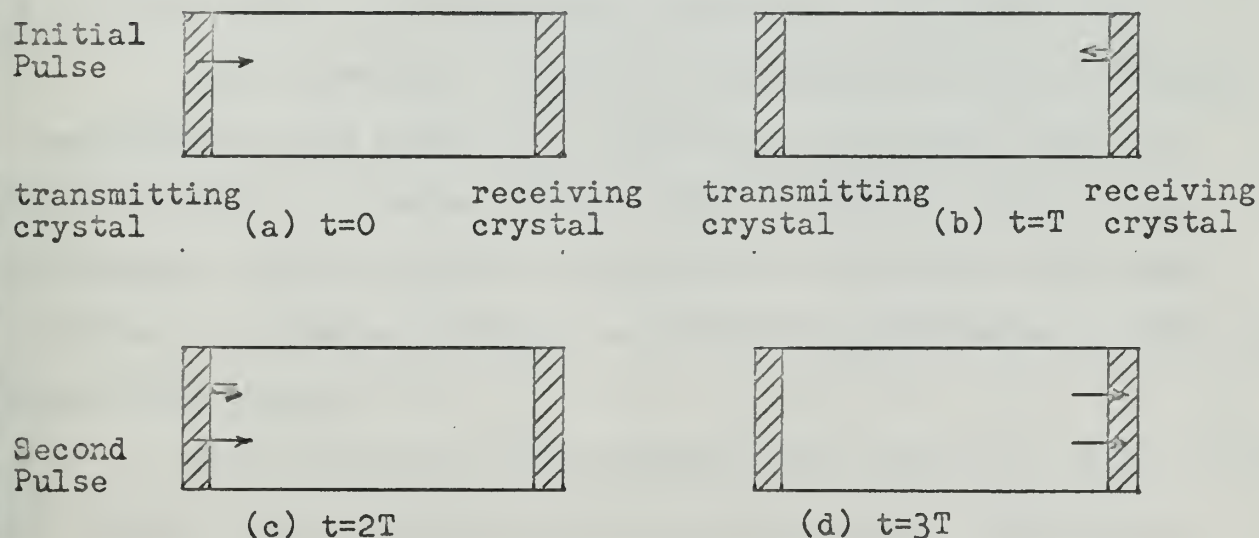


Fig. 1



Sound pulses are introduced at  $t = 0$  and  $t = 2T$  and are detected by a second transducer at the opposite end of the velocimeter. The time  $T$  can be adjusted so that the two pulses will arrive at the receiving transducer at the same time (Fig. 1). The repetition rate was adjusted so that the two pulses add for a maximum amplitude.

Looking at Fig. 1, a and c, we see that the repetition rate is the reciprocal of the time required for the pulse to travel twice the length of the velocimeter, so that  $c = \frac{2l}{(2T)} = 2lv$ .

#### B. Description of equipment

The equipment required to measure the velocity of sound as a function of temperature and pressure divides naturally into four systems.

The pressure system provides and regulates pressures up to 2000 psi which can accurately be measured to within 2 psi.

The temperature control and measurement system provides a temperature range from  $46^{\circ}\text{C}$  to  $523^{\circ}\text{C}$  for the sample when the pressure vessel is placed inside a high temperature oven. The measurement system consists of a platinum resistance thermometer connected to a Mueller bridge. A spotlight galvanometer is used to balance the bridge.

The electronic system produces the electrical pulses that are changed into the sound pulses by a transducer, accurately measures the repetition frequency of the pulses, and displays the received pulses on an oscilloscope to allow a correct superposition to be made.



The pressure vessel and components consist of the velocimeter and associated equipment, and a container to allow pressure to be put on the sample.

1. Pressure system:

A pressure line from the vessel leads to a Heise-Bourdon tube gauge and to a dry nitrogen tank which provides pressures up to 2200 psi. The pressure in the vessel is adjusted by a standard high pressure regulator. The system also has a provision for allowing air evacuation of the pressure vessel by a vacuum pump.

2. Temperature control and measurement:

The platinum resistance thermometer is placed in the receptacle provided in the base of the pressure vessel. This position inside the metal tends to average the temperature fluctuations of the oven and also permits a temperature reading near the sample. The galvanometer used with the Mueller bridge is a high sensitivity spotlight type. It has an internal resistance of 78 ohms, sensitivity of  $0.005 \mu\text{amp/mm}$ , and a period of 4.3 sec.

3. Electronic system:

A sine wave audio-oscillator provides the signal which eventually (when appropriately modified) excites the quartz transducer. The frequency (repetition rate) of the oscillator is accurately counted by an electronic counter. The sine wave passes through a band pass filter into special electronic pulse-shaping units. The band pass filter reduces electrical line interference that affects the display on the oscilloscope. The power supply for the special electronic pulse-shaping units was a constant voltage

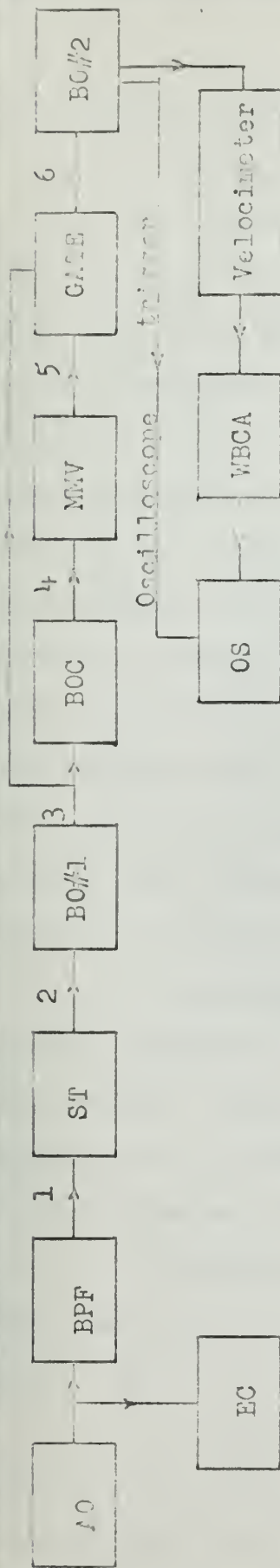




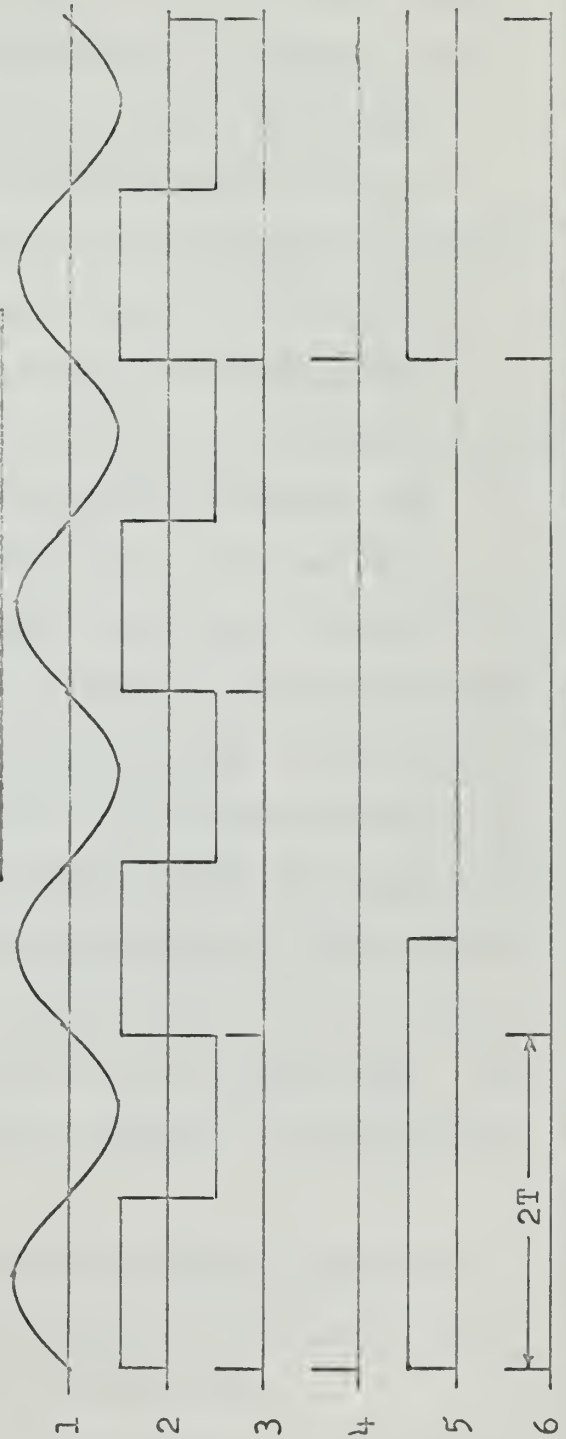
power supply. Direct current output was regulated to better than 1% over a range of 200 to 325 volts. An isolated AC voltage of 6.3 volts is also available for tube heater circuits. The sine wave is first led to a Schmidt trigger where a train of rectangular pulses is produced at the audio oscillator frequency. The shape of the various signals are shown in Fig. 2. The signal then goes to blocking oscillator #1 which produces spikes at the audio oscillator frequency. These spikes go to a blocking oscillator counter. The input signal is then used to excite an RC network which does not allow the device to pass any other input signals for a certain time interval. The time interval can be changed by external adjustments. This signal is then led to a monostable multivibrator. The output here consists of a series of rectangular pulses. The frequency of the audio oscillator is a multiple of this pulse frequency. This signal and the signal from blocking oscillator #1 are now led to a gate circuit. The signal from the multivibrator acts as a switch to allow a certain number of spikes (usually 2) from blocking oscillator #1 to go to the final blocking oscillator. The interval between these two spikes is  $2T$  and is determined by the frequency of the audio oscillator. The final blocking oscillator shapes the signal again, and the signal is sent to the transmitting transducer in the velocimeter. The signal from the receiving transducer is then amplified in the wide band chain amplifier and sent to the oscilloscope for display. The trigger input for the oscilloscope is taken from blocking oscillator #2.







Wave Forms at points indicated





#### 4. Pressure vessel and components:

The main component of the pressure vessel is the velocimeter. The quartz delay line in the velocimeter is manufactured from Amersill II quartz (an optical quality fused quartz)[see Fig. 3]. It is made in the form of a hollow cylinder with an outer diameter of about  $1 \frac{3}{16}$  in. and an inner diameter of  $\frac{5}{8}$  in. There is a hole  $\frac{1}{2}$  in. in diameter perpendicular to the drilled portion which is used for filling and emptying the delay line. The ends are polished while the other surfaces have a ground finish. The maximum and minimum lengths are diametrically opposed and measure 1.998995 and 1.998930 in., respectively. The maximum deviations of the ends from perfect planes are  $30$  and  $50 \times 10^{-6}$  in. The length of the delay line is greatest toward its center (around the bore). The linear thermal expansion coefficient  $\alpha$  for quartz is  $7.2 \times 10^{-7}/^{\circ}\text{C} \pm 10\%$  while the isothermal bulk compressibility  $K_T$  is  $18.6 \times 10^{-8}/\text{psi} \pm 7\%$ . These data were supplied by the manufacturer.

The transducers are  $1 \frac{3}{16}$  in. X-cut quartz discs with a  $\frac{3}{8}$  in. concentric disc of gold over chromium plated on one side. The metallic sample provides the electrode on the other side. All surfaces are polished and the fundamental frequency is designed to be approximately 5 Mc/sec.

The pressure vessel itself and the metallic components were machined from austenitic annealed stainless steel (type 321, 347). This type does not react with the metals used.

A pressure inlet is provided in the side of the vessel with a line leading to the pressure generating apparatus. An opening for the piezoelectric resistance capsule is provided in the



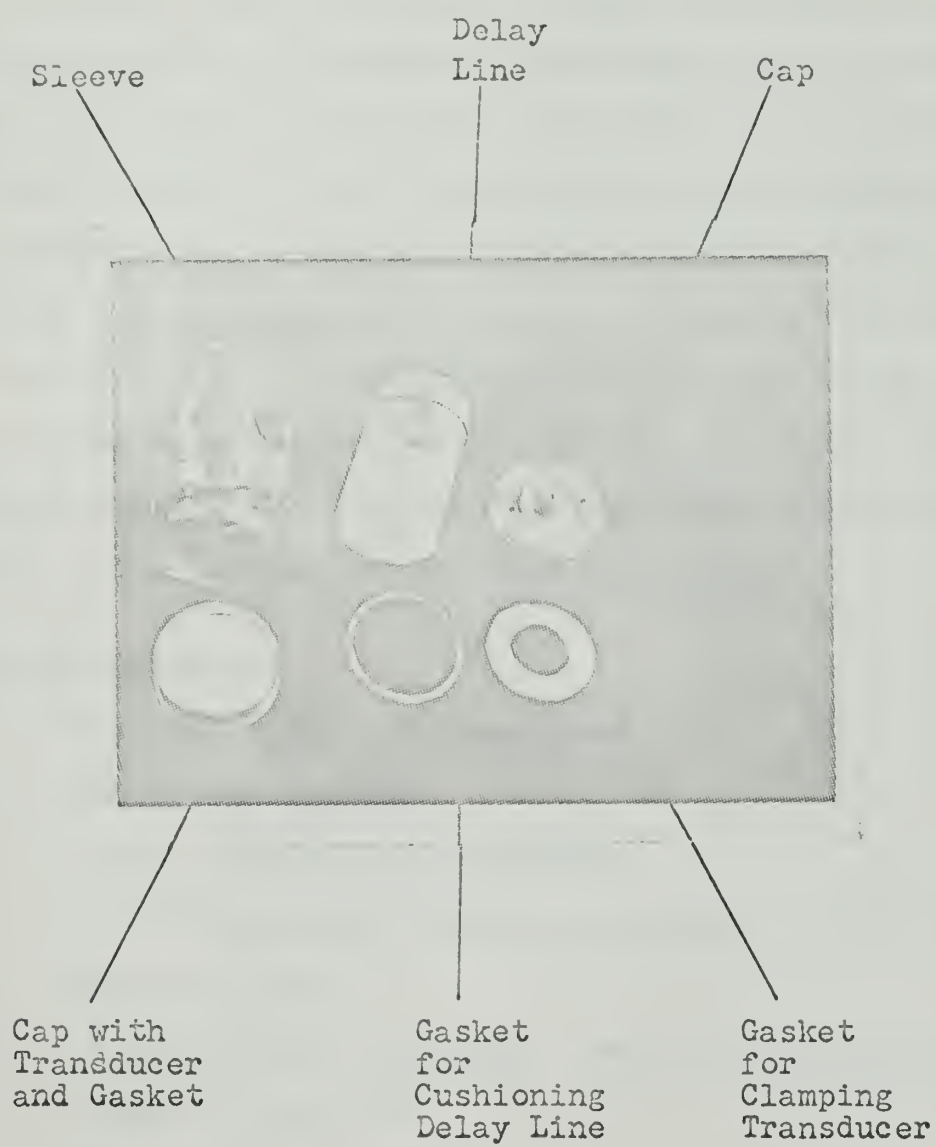


Fig. 3





solid material in the bottom of the pressure vessel.

The quartz delay line, cushioned by gaskets, is placed in a metallic sleeve (see Fig. 3). Caps containing electrical connections hold the transducers tightly against the delay line with the aid of a gasket to obtain clamped boundary conditions. A cup with a hole in its center is positioned over the opening in the side of the delay line so that the metal can run into the cavity upon melting. Since bismuth expands upon freezing, the above equipment must be able to rotate so that the metal can be poured from the openings in the delay line into a receptacle underneath the above parts. This assembly is attached to the pressure vessel's cover by electrical leads from the cover to the caps. An annealed copper gasket is used to seal the pressure vessel. The cover is then bolted to the pressure vessel.

5. List of equipment:

Pressure vessel and components

Composition gaskets

Mfr: Armstrong Cork Company

Asbestos-nitrile rubber composition An-890 Accopac

Pressure gauge

Heise-Bourdon Tube gauge temperature compensated;  
rated to 2000 psi

High pressure regulator

Mfr: Linde Division of Union Carbide Corporation

High pressure fittings and piping

Mfr: American Instrument Company





0380

0381

0382

0383

03831

03832

0384

03841

03842

0385

0386

03861

0387

0388

03881

Catalog in  
Thesis Coll.



High temperature oven

Mfr: American Instrument Company

Amico High Temperature Bench Mode Oven:

Catalog No. 4-3640

Temperature range:  $46^{\circ}\text{C}$  to  $523^{\circ}\text{C}$

Maximum temperature gradient:  $2^{\circ}\text{C}$

Temperature regulation:  $0.3^{\circ}\text{C}$

Platinum resistance thermometer

Mfr: Rosemount Engineering Company, Model 162D

Mueller resistance bridge

Mfr: Gray Instrument Company, Model S-1003

High sensitivity spotlight galvanometer

Mfr: Rubicon Division of Minneapolis-Honeywell

Regulator Company, Model 3432

Wide band chain amplifier

Mfr: Spencer, Kennedy Laboratories, Incorporated,

Model #202D, Bandwidth 100 kc to 200 Mc/sec.

with a voltage gain of  $20\text{ db} \pm 1\text{ db}$ .

Oscilloscope

Mfr: Fairchild Dumont, Type 766-H/P2B

X - Plug in unit

Type 74-13 delaying sweep with precision delay

X - plug in unit

Type 76-02 dual trace

Frequency response: DC to 25 mc/sec.

Amplitude: to 5 mv/cm.

Audio oscillator

Mfr: Hewlett Packard Company, Model: 200 CD



Electronic counter

Mfr: Hewlett Packard Company, Model 523 DR

Variable band pass filter

Mfr: Krohn-Hite Instrument Company, Model 320-A

Constant voltage power supply

Mfr: Associated Specialties Company, Model 3

Quartz delay line

Mfr: Amersil Quartz Division of Englehard Industries  
Incorporated

Transducers

Mfr: Valpey Corporation

#### C. Preparation of sample and experimental apparatus

The indium used was a sample that had been used previously in measurements of B/A, but since it had been used in the presence of a nitrogen atmosphere in a quartz and stainless steel container, it was considered reusable. The original metal had been obtained from the Indium Corporation of America with a guaranteed purity of 99.999%. The bismuth was obtained from Fisher Chemical Company (Cat. No. B-319) with an estimated purity of 99.98%. Analysis of the metal as certified by the supplier listed the following metallic impurities:

Arsenic (As)	0.0000%
Copper (Cu)	0.002 %
Iron (Fe)	0.001 %
Lead (Pb)	0.01 %
Antimony (Sb)	0.00 %



Before any data for the alloys were taken, sound velocity measurements were obtained for indium which agreed within 0.6 m/sec. and 0.005 m/sec-°C to that of Coppens.

Velocity measurements were made at four concentrations of bismuth. According to the Bi-In phase diagram, there are two eutectic and one peritectic points (at 34%, 66%, and 48% Bi respectively).<sup>3</sup> Data were recorded at these points and at a 17% Bi concentration. The latter point was studied in order to check on the approach of the alloy's characteristics to that of indium. Some measurements were also taken for bismuth.

Before any measurements were made, the experimental apparatus was first thoroughly cleaned with dilute nitric acid, water, benzene, and acetone rinses.

The first experimental sample was prepared by cleaning the metal as above except that the acid rinse was with a much weaker solution because the surface of the metal tended to oxidize. The metals were then weighed in order to determine and obtain the desired percentage alloy. They were then put into a beaker and heated under paraffin oil to about 300°C. The mixture was held at this point for about five minutes and was stirred vigorously. The alloy was then allowed to cool while the stirring continued. The freezing point of the alloy was determined roughly and checked with the phase diagram. The alloy was then cleaned with the above mentioned rinses and placed in the cup above the delay line.

Since indium is a fairly high priced metal, a technique of successive dilution was used. The samples were tested in order of increasing amounts of bismuth. After each sample had been tested, an appropriate amount of it was cleaned and weighed for the





next sample. The amount of bismuth necessary for the next concentration was put into a beaker with the required amount of the previous sample and the technique described above was again followed. The final sample was analyzed by Jarrell-Ash Company and found to have a concentration of 66.33% Bi. The computed percent bismuth was 67.00%. Therefore, the maximum error in any of the concentration values is considered to be about 1%. The computed concentrations were 17.00% Bi (hereafter designated as 17% Bi.), 33.84% Bi (hereafter designated as 34% Bi.), 47.66% Bi (hereafter designated as 48% Bi.), and 67.00% Bi (hereafter designated as 66% Bi.).

In order to get the acoustical signal into and out of the sample, a wetting agent was used. A silicone, Dow-Corning 200 fluid (cs 350, 12,500) served this purpose quite satisfactorily. The transducers were thoroughly cleaned with acid, benzene, and acetone rinses. They were then coated with the wetting agent. The coating had to be very thin in order not to influence the velocity data. In all cases the coating was thin enough so that interference patterns (Newton's rings) were seen. The components were then assembled and the whole assembly was placed in the oven. Electrical, pressure, and thermometric connections were made. Then the oven was brought slowly (to prevent warping of the pressure vessel) to the desired temperature. Air was evacuated from the vessel and nitrogen admitted. This was done to insure that the sample was in a nitrogen atmosphere and therefore its surface could not oxidize.



#### D. Equilibrium conditions

After the sample had melted (as indicated by the appearance of a transmitted signal on the oscilloscope), several hours were allowed to pass before any readings were taken. Since the thermometer was not in the sample, equilibrium conditions could only be determined by checking the change in repetition rate. A minimum of 3 hours was allowed to elapse between pressure readings and 8 hours between temperature readings. It was found that after 1 hour, the repetition rate had reached 90% of its final value, after 2 hours 99% of its final value; so that in a three hour period, the equilibrium error was well within r.m.s. reading error. An eight hour period was allowed to elapse for a temperature change. Data taken for a combination temperature and pressure change indicated that in a four hour period the repetition rate was 99% of the final rate.

#### E. Measurement of repetition rate and temperature

The readings were taken by adjusting the repetition rate so that the superposition of the two pulses at  $t = 3T$  (see Fig. 1) was a maximum. This procedure insured that the time between the pulses was the time required for one pulse to travel to one end and return. The wave packet at  $t = T$  was also displayed on the oscilloscope to aid in determining correct superposition. The frequency of the audio oscillator was then determined from the electronic counter. Temperature measurements were taken at this time also. Groups of ten frequencies and 7 temperature readings were taken together until the average of two groups of frequency agreed to within 0.1 cycle. The more consistent



readings were then used for calculations.

Results of using the above methods were satisfactory for all samples except bismuth. The high melting point of bismuth ( $271^{\circ}\text{C}$ ) caused the "wetting" agent to decompose. Four attempts were made to obtain data. The last attempt was the most successful. After six days above melting temperature, a signal of correct form appeared. However, the amplitude kept decreasing each day so that data for only three different temperatures were obtained.





### D. Superposition correction

The transmission coefficient for the transducer in the velocimeter is near zero for the air backed side and near unity for the sample side of the crystal. These values indicate energy is transferred very easily from the transducer and to the sample and back. A very short wave packet is therefore produced as the energy given the transducer by the electrical pulse is quickly dissipated into the sample. At the receiving transducer, interference may arise as some components of the wave packet arrive at the front of the transducer at the same time when some other components have reflected from the rear of the transducer. The interference effect can be computed by a straightforward analysis when the input is assumed to be a delta function.<sup>10</sup> The result of this calculation is shown for indium in Fig. 4.<sup>11</sup> An actual waveform for a sample composed of 66% Bi is shown superimposed on the computed values for pure indium. The curves almost coincide because the acoustic impedance for bismuth is  $1.67 \times 10^6$  while the acoustic impedance for indium is  $1.62 \times 10^6$  cgs units. Looking at the experimental curves we see the difference in amplitude to be slight between the first and second pulse which shows that one of Gol'dberg's required conditions ( $\alpha/E \ll 1$ ) is satisfied. Notice that the first  $1\frac{1}{2}$  cycles of the calculated and experimental pulse at  $t = 3T$  are completely missing, while the next half cycle is very small. This effect is the result of the interference mentioned above. Figure 4 can also be thought of as the picture of the pulse at  $t = 3T$ , the upper waveform being the second pulse introduced. To obtain a correct repetition rate, the pulses should be



### III. Corrections and Calibrations

The equipment's design provides a high degree of accuracy in measuring relative sound velocity in the delay line. However, errors in the absolute determination of the velocity of sound may arise from two different sources. The instruments such as the thermometer, pressure gauge, and electronic counter should be calibrated with the absolute values of their respective quantities so that absolute values of the sound velocity can be measured as a function of absolute quantities. The fact that measurements are taking place in a delay line instead of free space also influences these measurements. While some of these conditions are systematic and will not greatly affect the accuracy of the derivatives with respect to pressure and temperature, an attempt is made to correct for all possible errors.

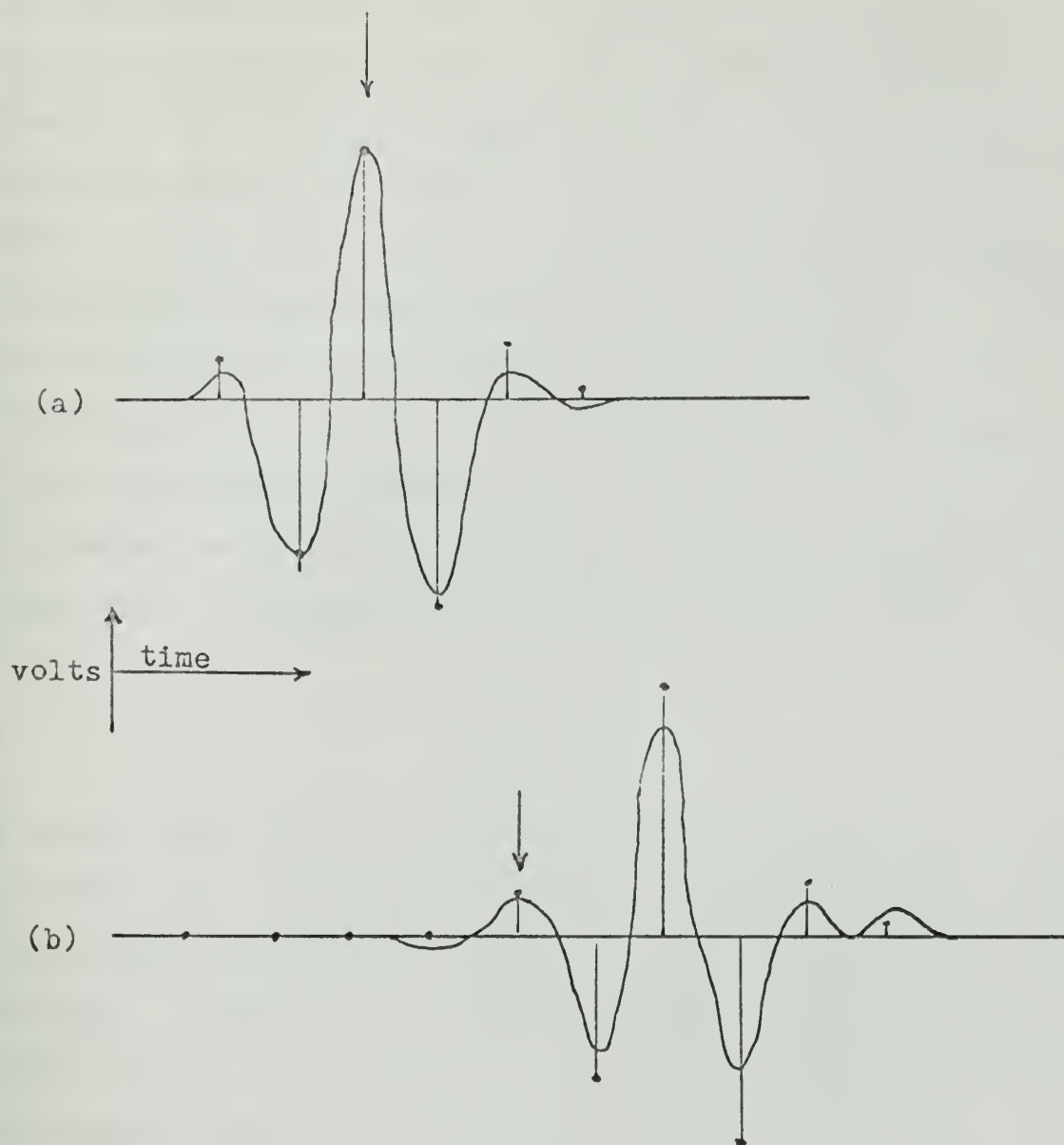
#### A. Delay line correction

Since the length of the delay line changes with temperature and pressure, an error is introduced thereby in the determination of the velocity. It can be shown that the length change is governed by the equation<sup>9</sup>

$$l = l_0 [1 + \alpha(t - 20^\circ\text{C})] [1 - \frac{1}{3} K_T p] \quad (4)$$

The maximum change in length of the delay line amounted to 0.0017 cm which caused a change of 0.5 m/sec in velocity. Because of the uncertainty in the values of  $\alpha$  and  $K_T$ , the maximum uncertainty due to this correction was about 0.003 m/sec.





- (a) Waveform of a pulse at  $t=T$   
 (b) Wavefore of the above pulse at  $t=3T$

The experimental wave packet is shown by the continuous lines (  $\cap$  ).

The calculated wave packet is shown by the heavy dots (  $\cdot$  ).

Fig. 4





superimposed as shown. The only pulses that could be added are the first half of the third cycle. The only error introduced by this superposition is due to waveguide effects. However, since these pulses are small, the changes in the sum of the amplitude is also small. Better accuracy can be obtained in finding a maximum amplitude by superimposing pulses of larger magnitude. Therefore, the pulses with the arrows drawn above were superimposed. A correction to the velocity of sound must now be made since the second pulse enters the delay line a certain time later in order to superimpose at the new position. Since the delay is one wavelength over a distance of  $2\ell$ , the correction to the sound velocity is

$$\Delta c = \frac{c\lambda}{2\ell} \quad (5)$$

$\Delta c$  varied from 5.225 to 9.664 m/sec, with an accountable uncertainty of 0.003 m/sec. One sound velocity measurement was taken using the correct superposition and compared to one using the above superposition. Differences in velocity amounted to 9.454 m/sec, all of which could be accounted for by equation (5) except for 0.210 m/sec. Experimental uncertainties amounted to 0.177 m/sec, so the unaccountable uncertainty this "incorrect" superposition introduces amounts to about 0.04 m/sec. This uncertainty is probably due to waveguide effects.

### C. Waveguide effect correction

Waveguide effects account for the next largest correction. When sound travels along a waveguide, the various frequency components travel at different speeds, depending on the





frequency. This produces a dispersive effect. The leading edge of each cycle does travel at the free field velocity, but since measurements were taken at maximum amplitude, this effect will cause a systematic error. The amount of this error can be calculated for a particular arrangement.<sup>12</sup> The error in the measured velocity of sound due to waveguide effects varied between 0.160 and 0.380 m/sec. The uncertainty introduced by this correction is negligible.

#### D. Viscosity correction

Viscous forces in a medium tend to slow the passage of sound waves. Kinsler and Frey state the expression for the velocity change  $\Delta c$  as<sup>13</sup>

$$\Delta c = c \left[ \frac{\mu}{4\pi\rho va^2} \right]^{\frac{1}{2}} \quad (6)$$

where  $\mu/\rho$  is kinematic viscosity,  $v$  is frequency of sound, and  $a$  is the radius of waveguide. This correction ranges from 0.100 to 0.049 m/sec. Values of kinematic viscosity were found only for indium,<sup>16</sup>  $\text{In}_2\text{Bi}$ <sup>15</sup>, and bismuth.<sup>17</sup> Values required for other concentrations were calculated from above values. Assigning an error of 50% to the value of kinematic viscosity used gives an estimated uncertainty of 0.004 m/sec here. Another possible source of error in the interpolated data may be the variation of viscosity with pressure,<sup>14</sup> but since no data could be found on its magnitude in liquid metals (in organic liquids, the viscosity roughly doubles for a pressure change from 1 to 2000 kg/cm<sup>2</sup>), no estimate was made. Since the viscosity correction is small and a 50% error was assumed in the value of kinematic viscosity, any variation due to pressure



should lie within these limits.

#### E. Temperature errors

The maximum temperature error is dependent on the accuracy of the calibration of the thermometer because the fluctuations in the reading of the bridge were within the accuracy of the calibration of the platinum thermometer.

#### F. Calibration

In order to determine the absolute velocity of sound as a function of temperature and pressure, the accuracy of the thermometer, pressure gauge, and electronic counter was checked against absolute values.

The platinum resistance thermometer was calibrated by Rosemount Engineering Company and found to be accurate to within  $\pm 0.015^{\circ}\text{C}$  from  $-183^{\circ}\text{C}$  to  $+350^{\circ}\text{C}$ .

The Mueller Bridge has a guaranteed accuracy of  $\pm 0.005\%$   $+0.00005$  ohms at a temperature of  $23 \pm 1^{\circ}\text{C}$ .

The Heise-Bourdon Gauge was calibrated with a dead weight piston gauge and found to be accurate within  $\pm 2$  psi.

The electronic counter was calibrated with WWV and adjusted for correct readings. It has a stability of two counts in one million per week and is accurate to  $\pm 1$  count.



IV. DataA. Sample calculation for velocity of sound.

A calculation is shown in detail below for one of the points of the 34% Bi sample. The experimentally determined data are:

Repetition rate  $20.76668 \pm 0.00077$  kc.

Temperature  $77.48 \pm 0.02^\circ\text{C}$

Pressure  $0 \pm 2$  psi

Actually the temperature is not determined directly, but is obtained from a table where resistance values are listed opposite the temperatures.

Corrections for changes in the length of delay line:

$$\begin{aligned} 2l &= 2l_0 [1 + \alpha(t - 20^\circ\text{C})] \left[1 - \frac{1}{3} K_{Tp}\right] & (4) \\ &= (10.154752 \text{ cm})(1.0000414)(1) \\ &= 10.155172 \text{ cm.} \end{aligned}$$

Hence

$$\begin{aligned} c &= 2lv = (10.155172 \text{ cm})(20.76668) \text{ kc.} \\ &= 2108.892 \text{ m/sec.} \end{aligned}$$

Correction for superposition:

$$\begin{aligned} \Delta c &= \frac{c\lambda}{2l} = \frac{c^2}{2fl} = \frac{(2108.892)^2}{(10.155172)(5 \times 10^6)} \\ &= 8.759 \text{ m/sec.} \end{aligned}$$





Correction for waveguide effects: <sup>12</sup>

$$\frac{\beta}{\omega} = \frac{(0.92)(x)}{a^2/\lambda}$$

x - Distance pulse travels

a - Radius of delay line

$\lambda$  - wavelength in medium

$$(\beta/\omega)_{x=15} = \frac{(0.92) x c}{(0.64)(5 \cdot 10^6)} = (4.35 \cdot 10^{-6}) c = 0.922171$$

$$\theta = \cot^{-1} \frac{\frac{1}{2}(\beta/\omega) - \frac{1}{48}(\beta/\omega)^3}{1 + \frac{1}{8}(\beta/\omega)} = 1.10003 \text{ radians}$$

$$wt'_0 = \frac{\frac{1}{8}(\beta/\omega)^2 + \theta}{1 + \frac{1}{48}(\beta/\omega)^3} = 1.195793$$

$$(\beta/\omega)_{x=5} = 0.307390 \quad \theta = 1.41709 \text{ radians}$$

$$wt'_0 = 1.428036$$

$$c = \frac{wt'_0}{3600} = 0.331 \text{ m/sec.}$$

Correction for viscosity:

$$\Delta c = c \left[ \frac{\mu}{4\pi\rho va^2} \right]^{\frac{1}{2}} = c \left[ \frac{1.0 \cdot 10^{-2}}{4\pi(5 \cdot 10^6)(0.64)} \right]^{\frac{1}{2}} = 0.042 \text{ m/sec. (6)}$$

Velocity of sound corrected for changes in length of delay line

2108.892 m/sec

Correction for superposition

8.759 m/sec

Correction for waveguide effect

0.331 m/sec

Correction for viscosity

0.042 m/sec



Error due to uncertainties in temperature and pressure corrections of delay line:	0.003 m/sec.
Error due to uncertainties in superposition correction:	0.003 m/sec.
Error due to uncertainties in viscosity correction:	0.004 m/sec.
Error due to root mean square deviations in obtaining repetition rates:	0.078 m/sec.
Corrected sound velocity	2117.362 $\pm$ 0.088 m/sec.

The experimentally determined sound velocities of the 17% Bi concentrations are given in Table I. The results of the calculations for each set of concentrations with the same pressures were fitted by a least squares method to polynomial equations by the Brown University IBM 7070 computer. The results of the computation for the sound velocity of the 17% Bi sample are also given in Table I below the experimental values of  $c$ . Polynomial curves of degree one through three were calculated. The linear least square fit resulted in a smaller root mean square deviation from the experimental points of the 17% Bi alloy than the second and third degree polynomial equations while the second degree polynomial least square fit resulted in smaller r.m.s. deviations from the experimental points of the 34% Bi, 48% Bi, and 66% Bi alloy than the first and third degree polynomials. However, there was still quite a large curve fitting error, even larger than experimental error in some cases.

Table II, which tabulates sound velocity as a function of temperature and pressure was computed from the polynomial



equations in the case of the alloys. For bismuth, the points given are the experimental results.





TABLE I

Table of values for the velocity of sound in a 17% Bi-In liquid alloy corrected for superposition errors, viscosity errors, and waveguide effects.

<u>0 psi</u>						
Temp (°C)	125.41	137.07	147.90	159.35	180.12	201.95
Ex. Velocity (m/s)	2222.367	2219.067	2216.175	2213.100	2207.452	2201.492
*Comp. "	2222.308	2219.137	2216.195	2213.079	2207.431	2201.495
<u>500 psi</u>						
Temp (°C)	125.41	136.87	147.91	158.84	180.00	201.84
Ex. Velocity (m/s)	2222.840	2219.955	2216.806	2213.797	2207.994	2202.033
Comp. "	2222.954	2219.818	2216.796	2213.805	2208.015	2202.038
<u>1000 psi</u>						
Temp (°C)	125.49	136.88	147.99	158.81	179.95	201.84
Ex. Velocity (m/s)	2223.424	2220.429	2217.250	2214.310	2208.547	2202.546
Comp. "	2223.	2220.340	2217.296	2214.332	2208.540	2202.543
<u>1500 psi</u>						
Temp (°C)	125.56	148.03	158.62	179.93	201.84	
Ex. Velocity (m/s)	2223.817	2217.807	2214.847	2209.079	2203.072	
Comp. "	2223.859	2217.744	2214.861	2209.062	2203.098	
<u>2000 psi</u>						
Temp (°C)	125.58	147.83	158.61	179.95	201.86	30
Ex. Velocity (m/s)	2224.362	2218.297	2215.353	2209.497	2203.570	
Comp. "	2224.360	2218.290	2215.350	2209.528	2203.551	

\*Values computed from the polynomial fitted to the experimental points.





TABLE II

Values of the velocity of sound (meters/sec.) as determined from the polynomial fitted to the experimental points.

## 17% Bi (by weight)-In alloy

Temp °C	Pressure (Psi)				
	0	500	1000	1500	2000
125	2222.419	2223.066	2223.595	2224.012	2224.518
143	2217.525	2218.140	2218.663	2219.113	2219.608
161	2212.630	2213.214	2213.732	2214.214	2214.698
180	2207.464	2208.015	2208.527	2209.043	2209.515
202	2201.482	2201.994	2202.500	2203.055	2203.513

## 34% Bi (by weight)-In alloy

77	2117.485	2117.972	2118.558	2119.045	2119.532
98	2113.580	2114.118	2114.641	2115.151	2115.665
125	2108.281	2108.869	2109.364	2109.882	2110.404
143	2104.573	2105.186	2105.696	2106.204	2106.717
161	2100.727	2101.357	2101.907	2102.394	2102.885

## 48% Bi (by weight)-In alloy

98	2013.542	2014.024	2014.584	2015.176	2015.711
125	2010.789	2011.219	2011.835	2012.431	2012.933
143	2008.535	2008.953	2009.607	2010.182	2010.676
161	2005.945	2006.370	2007.061	2007.599	2008.094
180	2002.847	2003.300	2004.030	2004.510	2005.017
194	2000.325	2000.812	2001.356	2001.995	2002.517

## 66% Bi (by weight)-In alloy

113	1893.969	1894.528	1895.121	1895.753	1896.378
125	1892.941	1893.524	1894.146	1894.779	1895.398
143	1891.098	1891.705	1892.360	1892.986	1893.598
161	1888.893	1889.511	1890.184	1890.796	1891.401
180	1886.174	1886.787	1887.463	1888.052	1888.654
194	1883.912	1884.414	1885.180	1885.745	1886.347
219	1879.329	1879.887	1880.517	1881.029	1881.633



Temp C	Pressure (Psi)				
	0	500	1000	1500	2000
Bismuth					
318	1639.433	1640.174	1640.943	1641.866	1642.542
328	1637.768	1638.552	1639.206	1639.927	1640.612
341	1637.040	1637.647	1638.191	1638.991	
357	1633.933				

Since the errors for all but the deviations when obtaining repetition rates are very small, they can be considered the same for all points. The r.m.s. error varied from about 0.030 m/sec to a maximum of 0.075 m/sec. The curve fitting error also varied widely from a negligible error up to 0.137 m/sec with an average of 0.52 m/sec.

From earlier discussion:

Error due to uncertainties in

temperature and pressure corrections: 0.003 m/sec.

Error due to uncertainties in super-

position corrections: 0.003 m/sec.

Error due to uncertainties in viscosity

correction: 0.004 m/sec.

Error due to root mean square deviations

in obtaining repetition rates:

Average 0.075 m/sec. Maximum 0.116 m/sec.

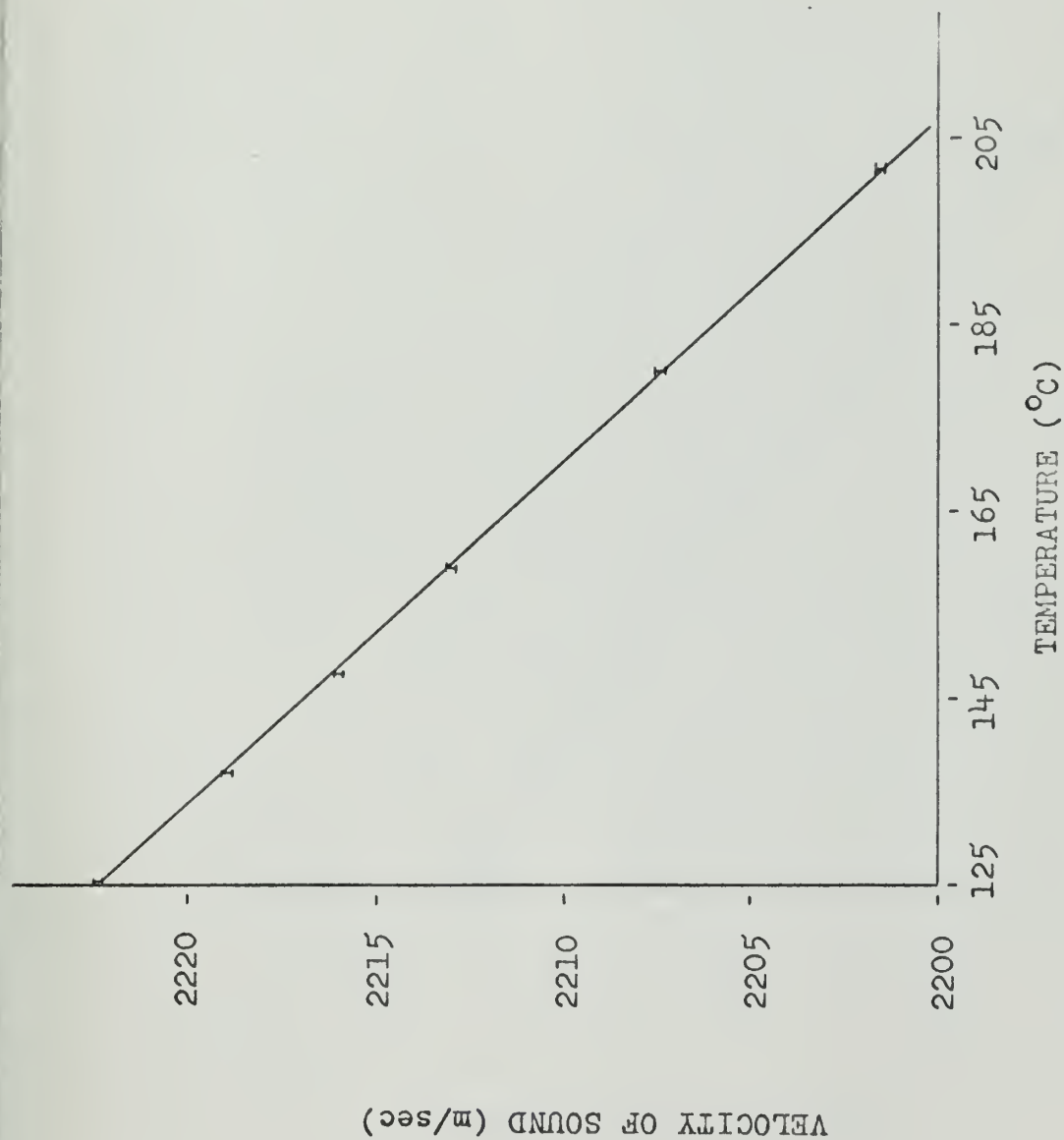
Total error of experimental points

Average 0.085 m/sec. Maximum 0.126 m/sec.

Maximum curve fitting error 0.137 m/sec.

Average curve fitting error 0.052 m/sec.



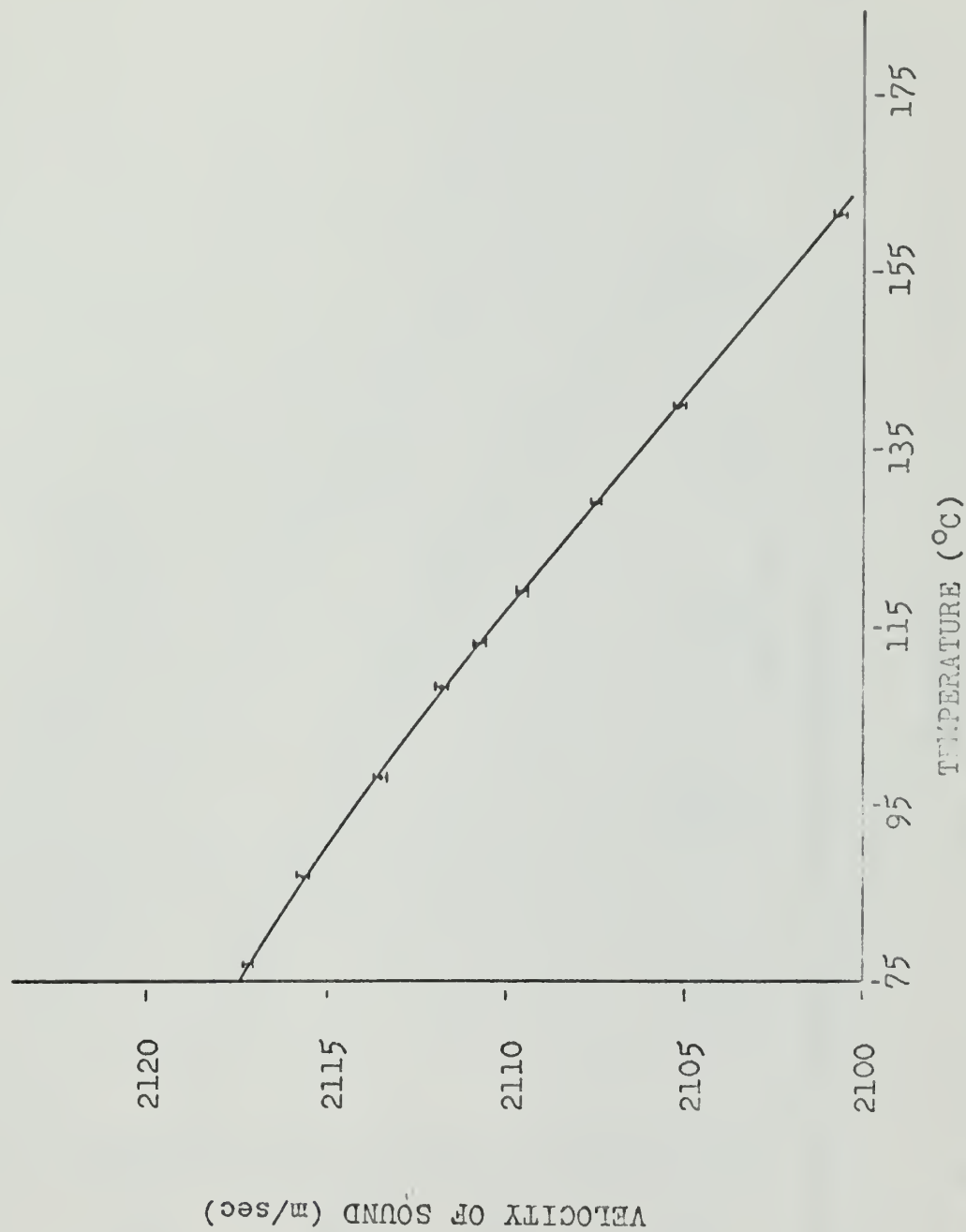


Temperature Dependence of Sound Velocity in a 17%Bi (by wt.)-In Alloy at 0 psi

GRAPH 1



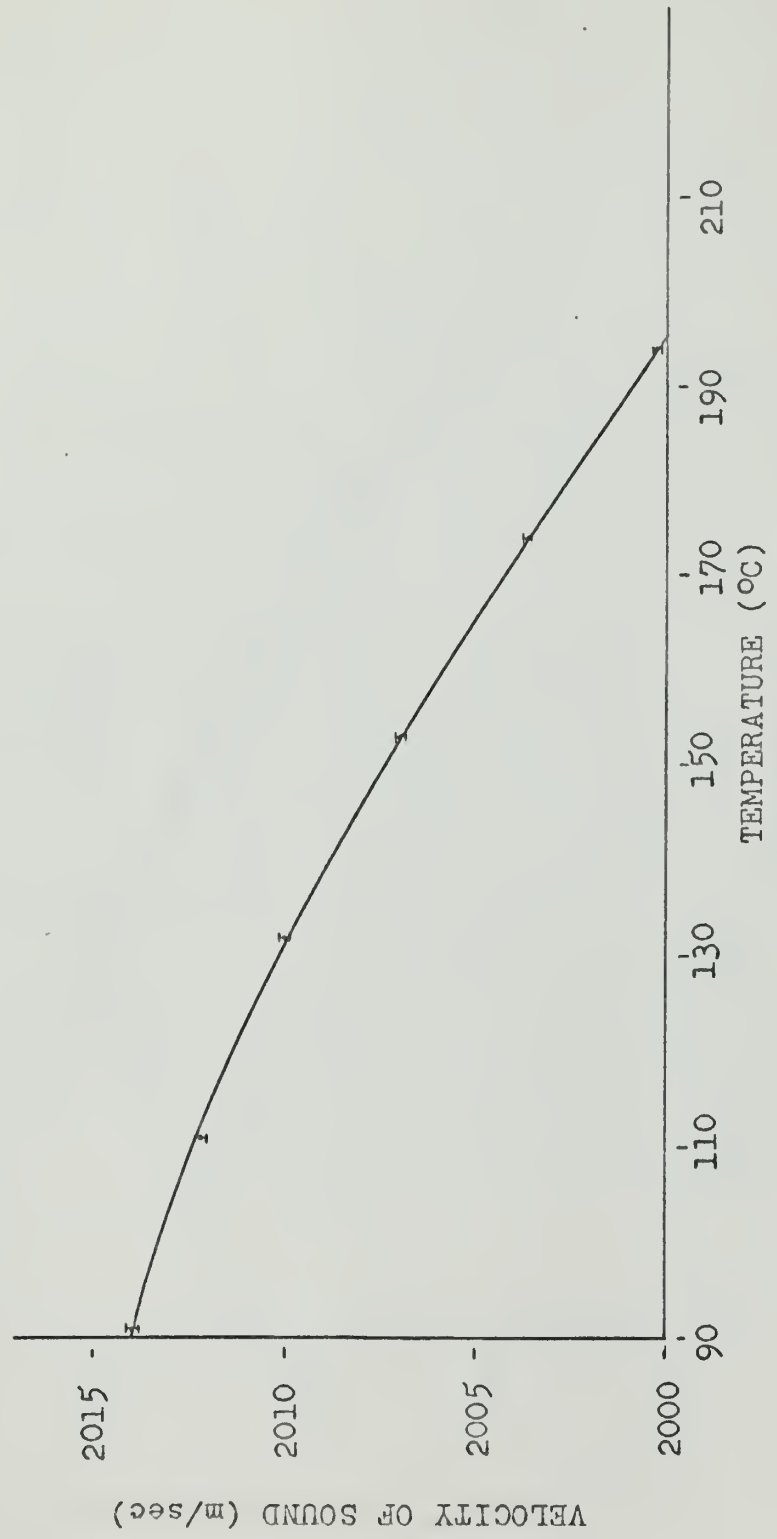




GRAPH 2

Temperature Dependence of Sound Velocity in a 3 1/4% Bi (by wt.)-In Alloy at 0 psi

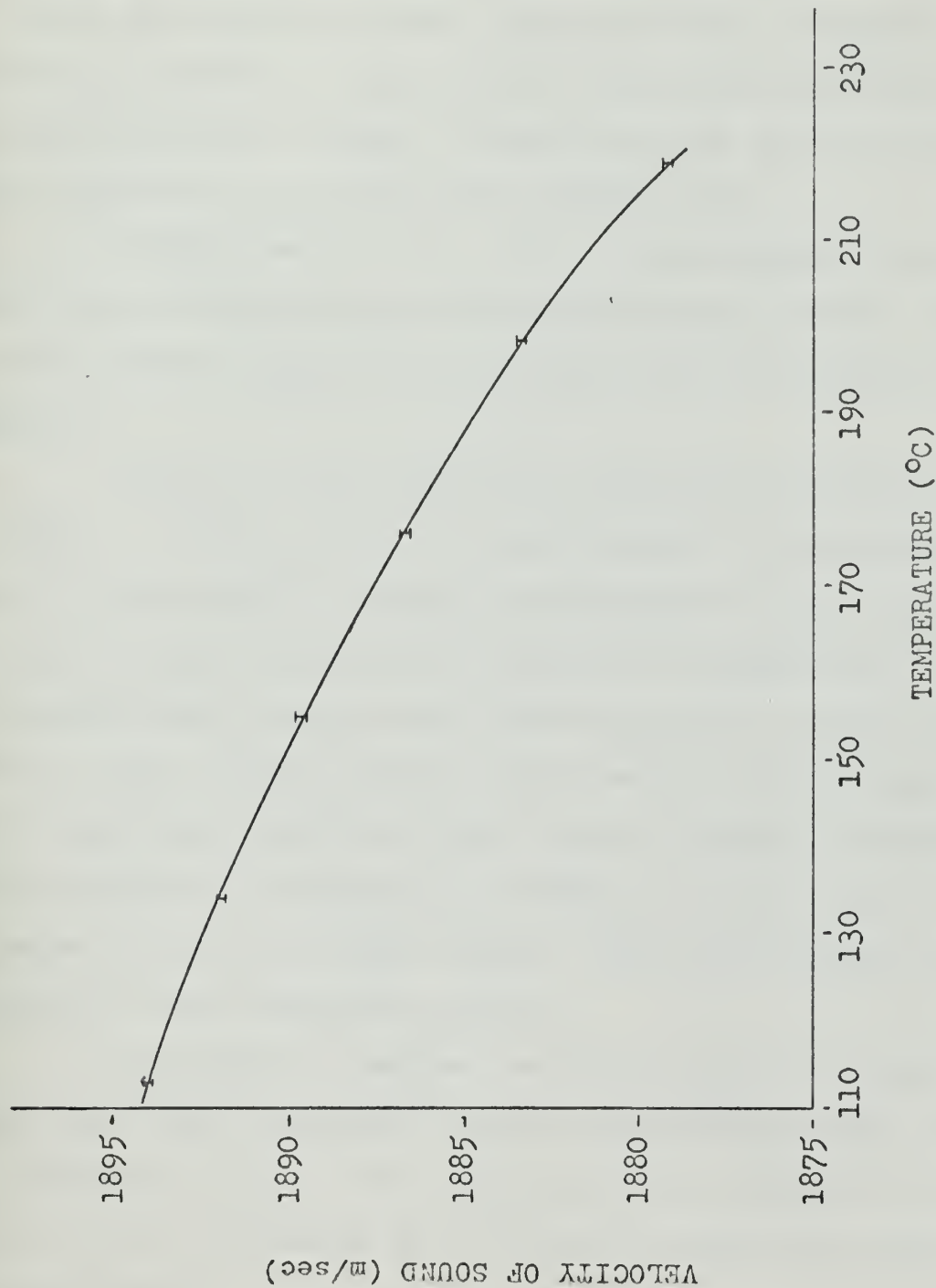




Temperature Dependence of Sound Velocity in a 48%Bi-In (by wt.) Alloy at 0 psi

GRAPH 3





Temperature Dependence of Sound Velocity in a 66%Bi (by wt.)-In Alloy at 0 psi

GRAPH 4



### C. Computation of B/A

After the equations of sound velocity at constant pressure were determined as a function of temperature, equations for sound velocity at constant temperature were determined as a function of pressure. These curves were plotted and found to have a linear dependence. Graph V shows the curve with the maximum slope and Graph VI the curve with minimum slope.

Beside the value of  $c$  and its derivatives, the computation of  $B/A$  required three experimentally determined values. These are density, thermal expansion coefficient, and heat capacity of the samples.

Values for the density of liquid In-Bi mixtures could not be found. A density curve vs. %Bi (by weight) at room temperature (i.e. for the solid)<sup>18</sup> showed an approximately linear relation. Equations to find density as a function of temperature<sup>17</sup> were extrapolated and density values computed using a linear relation. However, since bismuth expands upon freezing and the freezing point of all the alloys tested was below that of bismuth, an attempt was made to determine the density and change of density as a function of temperature for the 66%Bi sample. The data obtained agreed roughly with the calculated values.

The thermal expansion coefficient was not found for the alloys, but since indium and bismuth each have the same value for<sup>20</sup> the coefficient and the term containing this quantity is by far the smaller of the two making up  $B/A$  (Eq.3a), negligible error should be introduced here.

Heat capacity ( $C_p$ ) values for the alloys also were unavailable. A linear dependence variation between the values



# THEORY

1.

The first part of the theory is the definition of the system.

2. 3.

The second part of the theory is the definition of the system.

The third part of the theory is the definition of the system.

4. 5.

The fourth part of the theory is the definition of the system.

The fifth part of the theory is the definition of the system.

The sixth part of the theory is the definition of the system.

6.

The seventh part of the theory is the definition of the system.

The eighth part of the theory is the definition of the system.

The ninth part of the theory is the definition of the system.

The tenth part of the theory is the definition of the system.

The eleventh part of the theory is the definition of the system.

The twelfth part of the theory is the definition of the system.

The thirteenth part of the theory is the definition of the system.

The fourteenth part of the theory is the definition of the system.

The fifteenth part of the theory is the definition of the system.

7. 8.

The sixteenth part of the theory is the definition of the system.

The seventeenth part of the theory is the definition of the system.

The eighteenth part of the theory is the definition of the system.

The nineteenth part of the theory is the definition of the system.

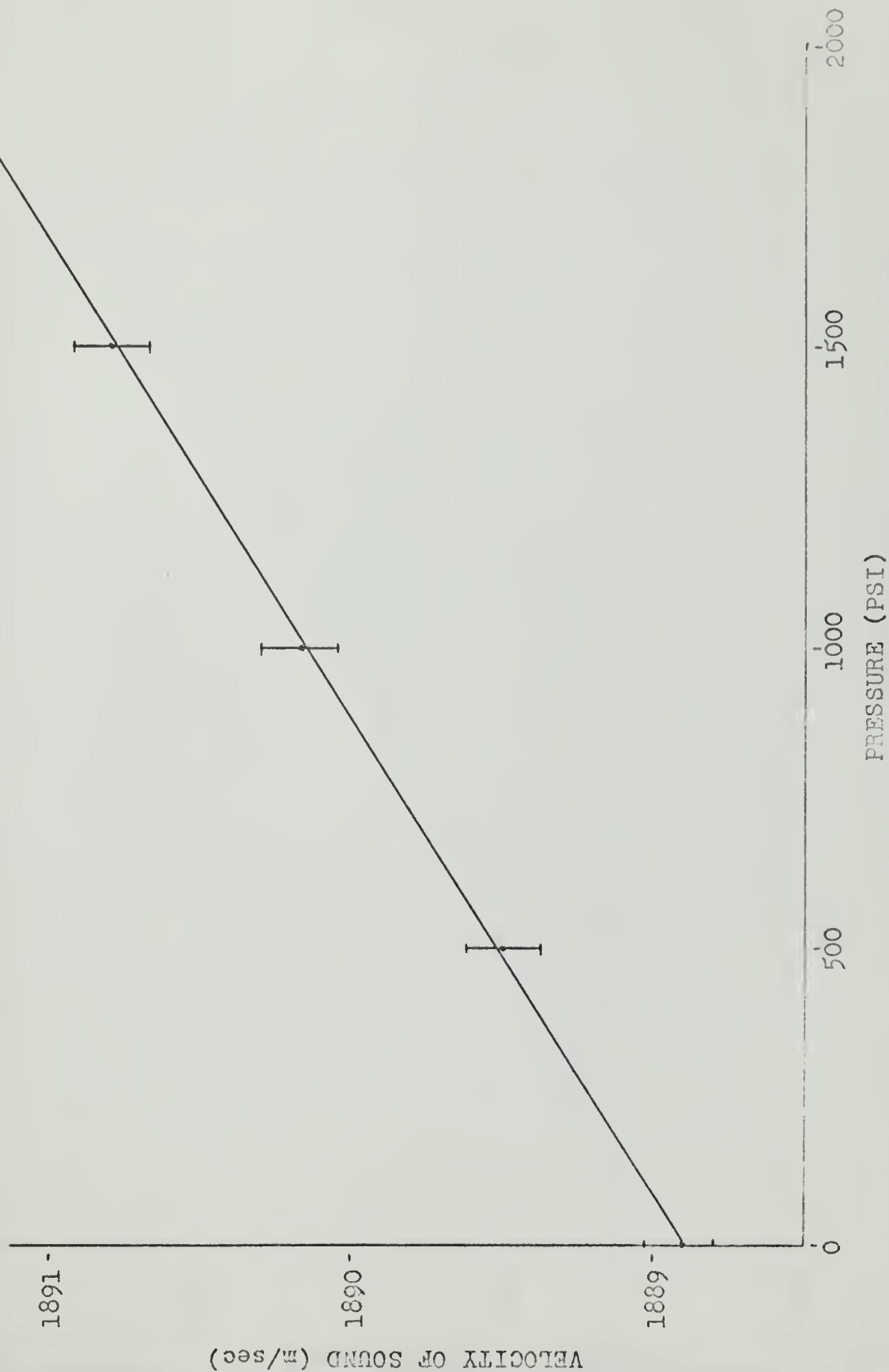
The twentieth part of the theory is the definition of the system.

9. 10.

The twenty-first part of the theory is the definition of the system.

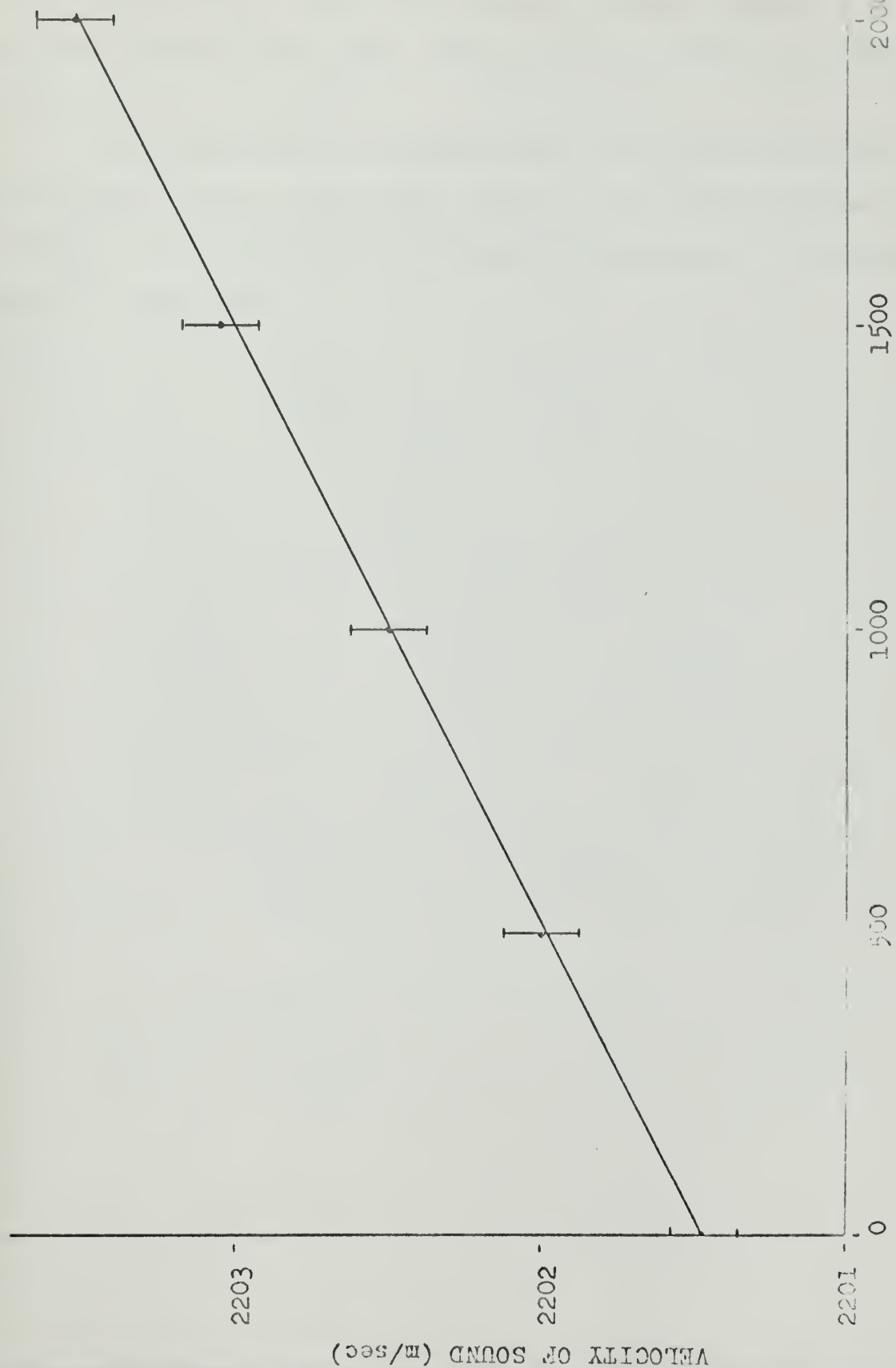
The twenty-second part of the theory is the definition of the system.

GRAPH 5





GRAPH 6





found for bismuth and indium was therefore used.<sup>17</sup> Any error in this value should have a very small effect as it is also in the smaller term of  $B/A$ .

The results of the calculations for density and heat capacity are listed in Table IV. Values of  $B/A$  were computed from the values listed in Table IV according to equation (3), and are tabulated in the table.





TABLE IV

Values of the Parameter of Non-linearity (B/A)

$\rho$	$\rho$	$c$	$(\partial c / \partial p) \times 10^3$	$\beta$	$c_p$	$(\partial c / \partial t)$	(B/A)'	(B/A)"	(B/A)
$C$	$(\text{gm/cm}^3)$	(m/sec)	(m/sec-psi)	$(10^{-4}/^\circ\text{C})$	$(\text{cal/gm}^\circ\text{C})$	(m/sec $^\circ\text{C}$ )			
17%Bi (by weight) - In alloy									
125	7.61	2222.419	1.045	1.2	0.0572	-0.2719	5.12	-0.2410	4.38
143	7.59	2217.525	1.042	"	"	-0.2737	5.09	-0.2549	4.34
161	7.57	2212.630	1.034	"	"	-0.2740	5.02	-0.2639	4.76
180	7.56	2207.464	1.026	"	0.0571	-0.2722	4.97	-0.2733	4.70
202	7.54	2201.482	1.016	"	"	-0.2728	4.89	-0.2866	4.60
34%Bi (by weight) - In alloy									
77	8.20	2117.485	1.024	1.2	0.0531	-0.1815	5.16	-0.1455	5.01
98	8.17	2113.580	1.043	"	"	-0.1905	5.22	-0.1613	5.06
125	8.15	2108.281	1.062	"	0.0530	-0.2021	5.29	-0.1834	5.11
143	8.14	2104.573	1.072	"	"	-0.2099	5.33	-0.1990	5.13
161	8.11	2100.727	1.079	"	0.0529	-0.2176	5.33	-0.2151	5.11
48%Bi (by weight) - In alloy									
98	8.29	2013.542	1.085	1.2	0.0495	-0.0879	5.25	-0.0761	5.17
125	8.27	2010.789	1.072	"	"	-0.1159	5.17	-0.1076	5.06
143	8.26	2008.535	1.071	"	"	-0.1345	5.15	-0.1303	5.02
161	8.23	2005.945	1.075	"	0.0494	-0.1532	5.15	-0.1547	5.00
180	8.21	2002.847	1.127	"	"	-0.1792	5.37	-0.1888	5.18
194	8.20	2000.325	1.096	"	"	-0.1874	5.21	-0.2032	5.01



TABLE IV (Cont'd.)

Temp C	$\rho$ ( $\text{gm/cm}^3$ )	$c$ (m/sec)	$(\partial c/\partial p) \times 10^3$ (m/sec-psi) ( $10^{-14}/^\circ\text{C}$ )	$\beta$ $c_p$ (cal/gm $^\circ\text{C}$ )	$(\partial c/\partial t)$ (m/sec $^\circ\text{C}$ )	(B/A)'	(B/A)"	(B/A)
66% Bi (by weight) - In alloy								
113	9.23	1893.969	1.205	1.2	0.0447	-0.0789	-0.0741	6.04
125	9.22	1892.941	1.229	"	"	-0.0923	-0.0892	6.13
133	9.20	1891.098	1.250	"	"	-0.1124	-0.1135	6.20
161	9.18	1888.893	1.254	"	"	-0.1325	-0.1394	6.16
180	9.16	1886.174	1.240	"	"	-0.1537	-0.1686	6.04
194	9.15	1883.912	1.218	"	0.0446	-0.1694	-0.1916	5.90
219	9.11	1879.329	1.152	"	"	-0.1973	-0.2345	5.49
Bismuth								
318	10.03	1639.433	1.555	1.2	0.0340	-0.157	-0.258	7.1



The error in determining  $B/A$  for the alloys is mainly the uncertainty of the values of  $(B/A)'$  since  $(B/A)''$  has an order of magnitude equal to the uncertainty of  $(B/A)'$ . Due to the estimated error in the density values ( $\pm 0.5$  gm), an uncertainty of 0.15 is calculated for  $B/A$ . The uncertainties in velocity are very small as the maximum uncertainty introduced to  $B/A$  is 0.00008. The uncertainty in the slope of  $c$  vs. pressure affects the accuracy of  $B/A$  greatly since the slope of this line is very small. Errors in the data points on the order of  $\pm 0.1$  m/sec. will cause an uncertainty of 0.3 in  $B/A$ . The dependence of  $c$  vs.  $p$  appears to be linear well within experimental error, so this assumption was used in the computing uncertainties above. The use of the average value of r.m.s. errors and curve fitting errors resulted in an average uncertainty to  $B/A$  of 0.218. The use of the maximum values resulted in an uncertainty of 0.58.

The calculation for the uncertainty for bismuth follows the same procedure as above, with a much smaller uncertainty due to density and a much larger uncertainty due to the slope of  $c$  vs.  $p$  as data at only three temperature points were used.

#### Errors for alloys

Error in $(B/A)$ due to uncertainties of density	0.15	
Error in $(B/A)$ due to uncertainties of $c$	0.0008	
Error in $(B/A)$ due to uncertainties of $(\partial c / \partial p)_t$ (av)	0.218	(max.) 0.433
Total uncertainty in $(B/A)$	(av) 0.37	(max.) 0.58





Errors for Bismuth

Error in (B/A) due to uncertainties of density	0.09
Error in (B/A) due to uncertainties of c	0.0004
Error in (B/A) due to uncertainties of $(\partial c / \partial p)_t$	0.96
Total uncertainty in (B/A) for bismuth	1.2





## V. Conclusions

As far as could be determined there had been no previous work done in determining B/A for indium-bismuth alloys. B/A measurements for pure indium and velocity measurements for bismuth as a function of temperature have been reported. The available results with the appropriate results of this work are given below.

	Indium (Coppens) <sup>19</sup>	17% Bi-In Alloy (This work)
Temp (°C)	160	161
$(\partial c / \partial p)_T \times 10^{-6}$ (cm/dyne-sec)	1.47	1.49
$(\partial c / \partial t)_p$ (cm/sec-°C)	-28.5 $\pm$ 0.6	-27.4 $\pm$ 0.2
c (m/sec)	2313 $\pm$ 0.6	2212 $\pm$ 0.2
(B/A)'	4.78	5.02
(B/A)''	-0.23	-0.26
(B/A)	4.5 $\pm$ 5%	4.8

Bismuth			
Temp (°C)	Velocity (m/sec)	$(\partial c / \partial t)$ (m/sec°C)	(Source)
271	1635 $\pm$ 15	-0.5	(20)
285	1663 $\pm$ 5		(22)
289	1666	0	(21)
318	1639 $\pm$ 2	-0.16	(This work)

The results of this work appear to approach the values for indium as the concentration of indium is increased (see also Sections IV-B and D). The velocity of bismuth found in this research agrees with Kleppa's value if  $(\partial c / \partial t)_p$  found in this work is used to extrapolate to the temperature used. Otherwise the value lies between the two ranges of reported values.



It is possible that the sound velocity measurements reported here were made under non-equilibrium conditions or conditions which were not considered when making applicable corrections. For about six days after the sample had melted, the signal on the oscilloscope indicated poor acoustical contact of the sample with the transducers. Then the signal changed to one indicating good acoustical contact. However, the voltage amplitude of the signal started to decrease slowly, so that after five more days an accurate superposition could no longer be made. Upon disassembly of the pressure vessel and components, the transducers were found to be cracked. Bismuth had leaked out of the delay line and was found in the sleeve between the transducer and cap at one end of the velocimeter. The reason for loss of amplitude of the signal was probably due to this leakage of bismuth. The bismuth collecting behind the transducers may have affected some of the earlier assumptions used in computing corrections such as the assumptions of air-backed transducers, a filled delay line, and a fundamental resonating frequency of 5 Mc/s. The bismuth probably leaked through a crack in one of the transducers caused by thermal stresses set up by the high temperatures. Due to these uncertainties an error in velocity measurements of 2 m/s is assigned. A larger error is not considered reasonable because the waveform observed did agree very closely with the calculated waveform (see Section III-B), but since the set of velocity measurements was not completely consistent, the above estimate of error was made.

Kudriavtsev derived an expression for the velocity of sound in mixtures as a function of concentration of the components.<sup>23</sup>



Assuming an ideal mixture, we have

$$U = \mu U_1 + (1-\mu)U_2 \quad (7)$$

where  $U$  is the internal energy and  $\mu$  is the molar fraction of the first component. Also

$$v = \mu v_1 + (1-\mu)v_2$$

where  $v$  is the volume. Differentiating equation (7) twice with respect to volume at constant entropy and noting that

$$\left(\frac{\partial^2 U}{\partial v^2}\right)_S = - \frac{c^2 M}{v^2}$$

where  $M$  is the molecular weight and  $c$  is sound velocity, Kudriavtsev obtained

$$c^2 = \mu \frac{M_1}{\bar{M}} c_1^2 + (1-\mu) \frac{M_2}{\bar{M}} c_2^2$$

where  $\bar{M}$  is the average molecular weight. A plot of the above values of sound velocity is shown on Graph 7 along with the experimental results of Coppens and this work.<sup>24</sup> The maximum difference between values of  $c$  is 3%.

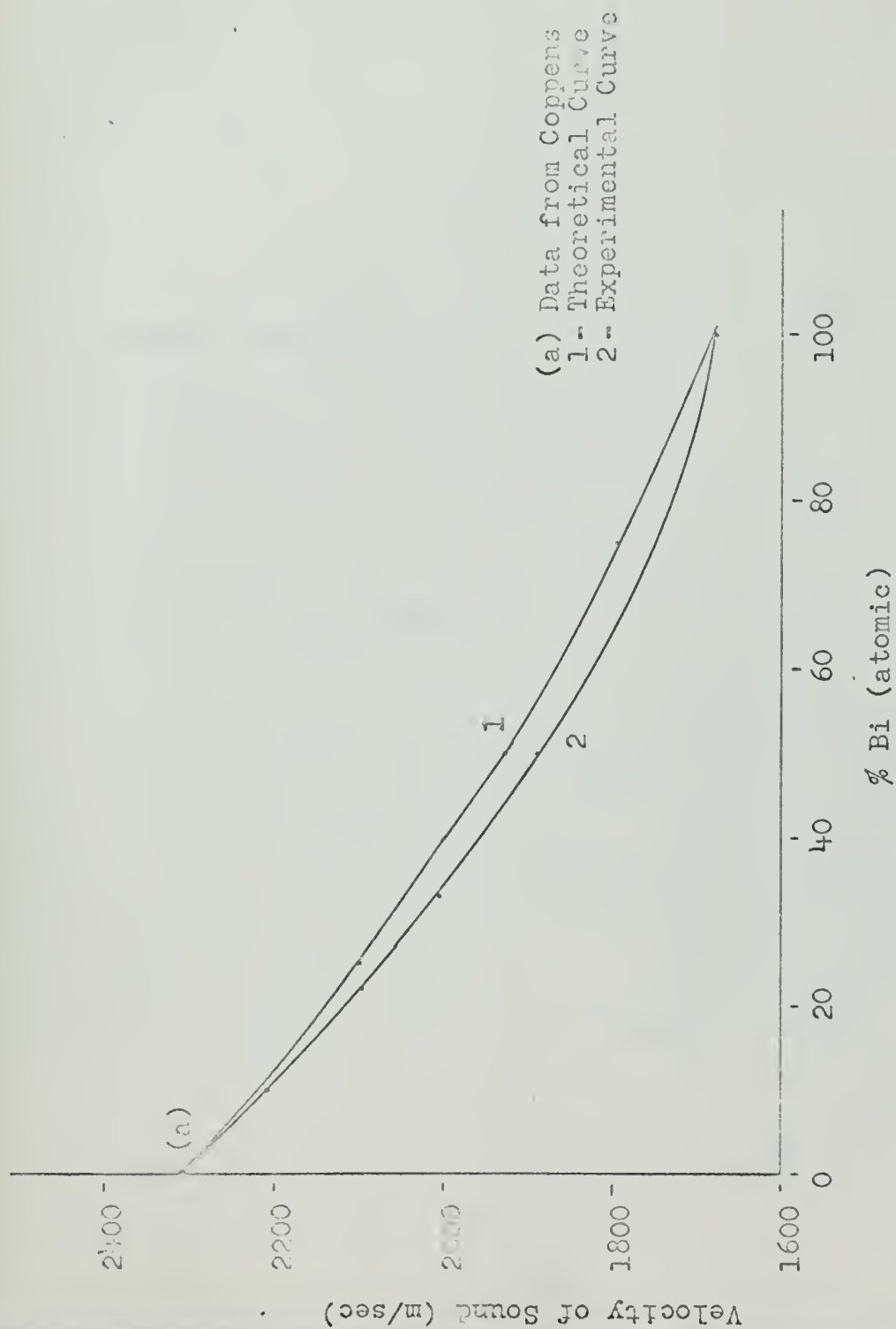
The reason the  $c$  vs. temperature dependence for three of the alloys has a varying slope is not known but may be due to the difference in slope for this dependence in the pure metals or may indicate a change in the slope of temperature dependence of bismuth beyond the range investigated.

The B/A data for the indium-bismuth system are shown on Graph 8. The values increase regularly with concentration with the exception of the 48% Bi alloy. The compound  $\text{In}_2\text{Bi}$  is formed, and a peritectic was found by Perotti in this area of concentration.





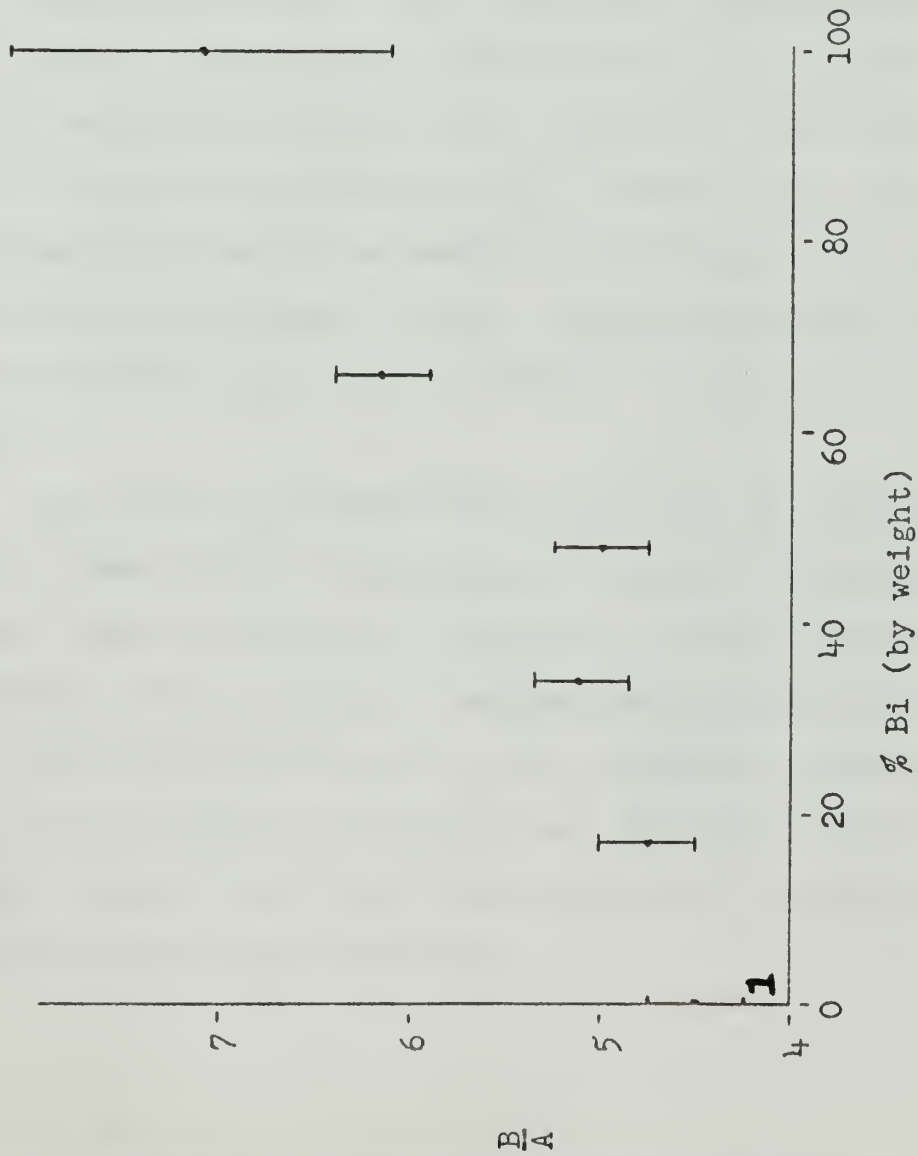
GRAPH 7



Dependence of sound velocity on composition in In-Bi alloy at  
161°C and 0 psi



1) Data point from Coppens<sup>24</sup>



% Bi (by weight)

Composition Dependence of B/A in In-Bi Alloy at 161°C



No other unusual characteristics have been reported.

The non-linear parameter of the equation of state  $p = p(\rho, s)$  has not been derived from first principles, nor has even a rough guide been established for predicting values. Thus far, experimental values have been obtained for some metallic elements, alloys, water, and various organic fluids. Reported values of  $B/A$  range from 2.7 to about 10.5.

There are a few physical constants that appear to be related to  $B/A$ . The metals provide a range of  $B/A$  values from 2.7 to 7.8. Physical constants that follow this trend are  $1/c$ ,  $1/\text{latent heat of vaporization}$ , and density (see Graph 9). However, when water and organic liquids were considered, the only physical constant to follow the trend was  $1/c$ . The fact that  $1/c$  appears to be proportional to  $B/A$  is somewhat surprising as in equation 3a, it is directly proportional to  $B/A$ . Acoustic impedance ( $\rho c$ ),  $\rho c^2$ , and  $B$  do not follow this trend. Table V lists some of these parameters.

The effect of temperature on  $B/A$  may be important in determining what physical mechanisms determine the degree of non-linearity. Water changes by a factor of 1.9 over the temperature range  $0^\circ\text{--}100^\circ\text{C}$ , while ethanol's maximum variation in  $B/A$  is 0.6.

The fact that there are less parameters that follow the trend of  $B/A$  for organic liquids is not considered unusual, because the organic molecules are much more complex so that combinations of other effects may be more important.



Physical Constants of Some Substances

Material	Temp (°C)	B/A	Velocity (m/sec)	Latent heat of vaporiza- tion (cal/gm)	Density (gm/cm <sup>3</sup> )	Isother- mal Compres- sibility (cm <sup>2</sup> /dyne)
Sodium	110	2.7 <sup>b</sup>	2521 <sup>b</sup>	1005 <sup>a</sup>	0.93 <sup>a</sup>	21.0 <sup>h</sup>
Tin	240	4.4 <sup>b</sup>	2470 <sup>b</sup>	573 <sup>a</sup>	6.95 <sup>a</sup>	3.1 <sup>h</sup>
Indium	160	4.5 <sup>b</sup>	2313 <sup>b</sup>	468 <sup>a</sup>	7.03 <sup>a</sup>	3.2 <sup>h</sup>
Water	10	4.6 <sup>c</sup>	1447 <sup>c</sup>	590 <sup>g</sup>	1.00 <sup>g</sup>	5.0 <sup>g</sup>
Bismuth	318	7.1	1639	204 <sup>a</sup>	10.03 <sup>a</sup>	
Mercury	30	7.8 <sup>b</sup>	1440 <sup>b</sup>	70 <sup>a</sup>	13.52 <sup>a</sup>	0.4 <sup>i</sup>
Benzene	30	9.0 <sup>d</sup>	1275 <sup>d</sup>	94@80° g	0.88 <sup>g</sup>	10.2 <sup>g</sup>
Acetone	20	9.2 <sup>d</sup>	1188 <sup>d</sup>	125@56° g	0.79 <sup>g</sup>	12.8 <sup>g</sup>
Methanol	0	9.5 <sup>d</sup>	1189 <sup>f</sup>	263@65° g	0.79 <sup>g</sup>	10.7 <sup>g</sup>
Methy- Acetate	30	9.7 <sup>d</sup>	1128 <sup>d</sup>	114@58° g	0.92 <sup>d</sup>	--
Diethy- lamine	30	10.3 <sup>d</sup>	1095 <sup>d</sup>	91@58° g	0.71 <sup>g</sup>	--
n-Propanol	0	10.5 <sup>d</sup>	1295 <sup>f</sup>	164@97° g	0.80 <sup>g</sup>	10.5 <sup>g</sup>
Ethanol	0	10.5 <sup>d</sup>	1232 <sup>f</sup>	204@78 g	0.79 <sup>g</sup>	9.9 <sup>g</sup>

a. Ref. 17

f. Ref. 28

b. Ref. 19

g. Ref. 29

c. Ref. 25

h. Ref. 20

d. Ref. 26

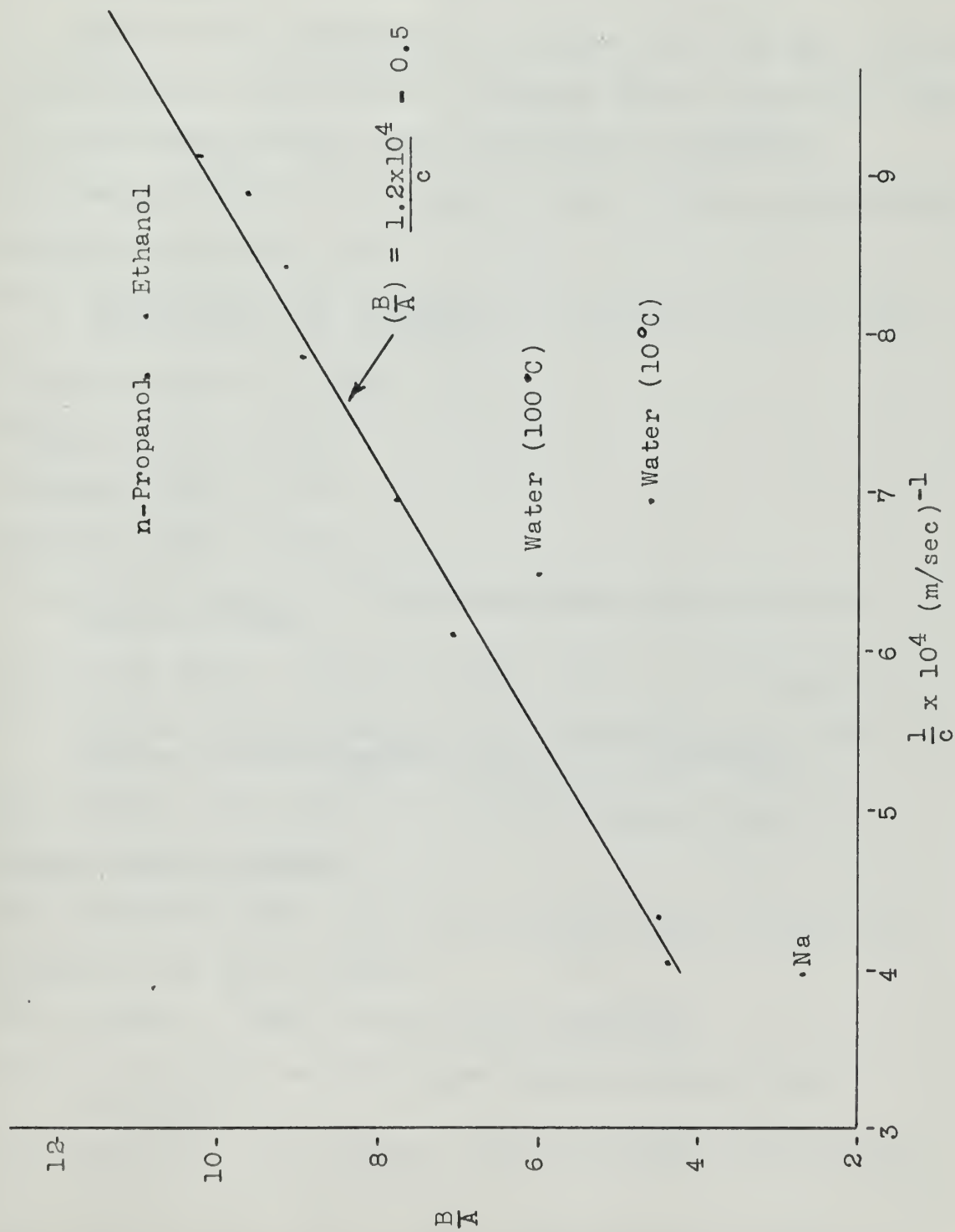
i. Ref. 13

e. Ref. 27





GRAPH 9

Dependence of  $B/A$  on the inverse of sound velocity



# References

1. V.V. Shklovskaya-Kordi, Soviet Phys. Acoustics 2, 821(1963).
2. L.K. Zarembo and V.A. Krasil'nikov, Soviet Phys. Uspekhi 2, 580(1959).
3. L. Adler and E.A. Hiedemann, J. Acoust. Soc. Am. 34, 410(1962).
4. Alan Coppens, p.103, Doctor's Thesis, Brown University (1965).
5. Z.A. Gol'dberg, Soviet Phys. Acoustics 2, 346(1956).
6. M. Greenspan and C.E. Tschiegg, J. Res. N.B.S., 59, 249(1957).
7. Coppens, loc. cit., p.27.
8. E.A. Peretti and S.C. Carapella, Jr., Trans. Am. Soc. Met. Preprint No. 29, (1948).
9. Coppens, loc. cit. p.89.
10. Coppens, Ibid., p.66.
11. Coppens, Ibid., p.54.
12. Coppens, Ibid., p.77.
13. L.E. Kinsler and A.R. Frey, Fundamentals of Acoustics, 2nd Ed. (1962).
14. R.H. Ewell and H. Eyring, J. Chem. Phys., 5, 734(1937).
15. Y.A. Dutchak, M.M. Klym, and A.G. Mykolauchuk, The Phys. of Metals and Metalography, 14, No. 5, 132(1962).
16. M.F. Culpin, Proc. Phys. Soc. (London) 20B, 1069(1957).
17. Liquid Metals Handbook.
18. P.W. Bridgman, Proc. Am. Acad. Arts Sci., 84, 43(1954-55).
19. Coppens, loc. cit., p.100.
20. O.J. Kleppa, J. Chem. Phys., 18, 1331(1950).
21. Z.L. Khodov, Phys. of Metals and Metalography 10, No. 5, 129(1960).
22. I.G. Polotskii, V.F. Taborov, and Z.L. Khodov, Soviet Phys. Acoustics 2, 36(1956).
23. B.B. Kudriavtsev, Soviet Phys. Acoustics 2, 36(1956).

the first of these is the fact that the system is not in equilibrium.

The second of these is the fact that the system is not in equilibrium.

The third of these is the fact that the system is not in equilibrium.

The fourth of these is the fact that the system is not in equilibrium.

The fifth of these is the fact that the system is not in equilibrium.

The sixth of these is the fact that the system is not in equilibrium.

The seventh of these is the fact that the system is not in equilibrium.

The eighth of these is the fact that the system is not in equilibrium.

The ninth of these is the fact that the system is not in equilibrium.

The tenth of these is the fact that the system is not in equilibrium.

The eleventh of these is the fact that the system is not in equilibrium.

The twelfth of these is the fact that the system is not in equilibrium.

The thirteenth of these is the fact that the system is not in equilibrium.

The fourteenth of these is the fact that the system is not in equilibrium.

The fifteenth of these is the fact that the system is not in equilibrium.

The sixteenth of these is the fact that the system is not in equilibrium.

The seventeenth of these is the fact that the system is not in equilibrium.

The eighteenth of these is the fact that the system is not in equilibrium.

The nineteenth of these is the fact that the system is not in equilibrium.

The twentieth of these is the fact that the system is not in equilibrium.

The twenty-first of these is the fact that the system is not in equilibrium.

24. Coppens, loc. cit., p.93.
25. R.T. Beyer, J. Acoust. Soc. Am. 32, 719(1960).
26. R.T. Beyer, private communication.
27. W.D. Wilson, J. Acoust. Soc. Am., 31, 1067(1959).
28. W.D. Wilson and D. Bradley, J. Acoust. Soc. Am. 36, 333(1964).
29. Handbook of Chemistry and Physics, 39th ed. (1957).
30. Coppens, loc. cit., p.16.















thesB201

An experimental determination of the par



3 2768 001 91244 7

DUDLEY KNOX LIBRARY